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(54) 【発明の名称】 光電変換素子

(57) 【要約】

【課題】 高い光電変換特性を有する有機色素を用いた色素増感光電変換素子を提供する。

【解決手段】 有機色素によって増感された半導体微粒子を用いる光電変換素子であって、半導体微粒子表面に対し垂直方向に色素発色団が複数個存在するように有機色素が吸着していることを特徴とする光電変換素子。ただし、金属多核錯体部分は一つの発色団とする。

PATENT ABSTRACTS OF JAPAN

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(54) PHOTOSEMICONDUCTOR ELECTRODEPHOTOELECTRIC CONVERSION DEVICE AND PHOTOELECTRIC CONVERSION METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a photosemiconductor electrode with excellent photoelectric conversion efficiency, stability and durability.
SOLUTION: A photosemiconductor electrode includes a chemical adsorbing membrane consisting of at least one type of compound represented by either formula (I): $(Y1)_mR1(COY2)_n$ formula (II): $(Y1)_mR1(NCO)_n$ or formula (III): $(T1)_mR1(Y3)_n$ reacting with a base material and a pigment membrane consisting of at least one type of pigment compound reacting with the chemical adsorbing membrane to form a covalent bond in sequence on the base material of a semiconductor where Y1 is a halogen atom-OR2 or -OCOR2 Y2 is a halogen atom-OH or -OCOR2 Y2 is a halogen atom-OH or -OR2 Y3 is -OH-NH2 or NHR2 Y4 is a halogen atom R1 is a saturated or unsaturated aliphatic hydrocarbon group aromatic hydrocarbon or heterocyclic group R2 is an aliphatic hydrocarbon aromatic hydrocarbon or heterocyclic group with the number of carbons being 1 to 20 and m and n are integers between 1 and 3 inclusive respectively.

CLAIMS

[Claim(s)]

[Claim 1] A chemical adsorption film by at least one sort of a compound expressed with either following formula (I) and (II) reacted to this substrate and (III) on a substrate of a semiconductor. An optical semiconductor electrode which has a coloring matter film by at least one sort of a pigment compound which reacts to this chemical adsorption film and can form a covalent bond in this order and is characterized by things. (Y¹)_mR¹(COY²)_n (Y¹) (I) _mR¹(NCO)_n (Y¹) (II) _mR¹(Y³)_n (III) however said formula (I) (II) and (III) Y¹ expresses halogen atom-OR²-OCOR²-OSO₂R²-COY⁴-COOR² or -(CO)₂O inside. Y² expresses a halogen atom-OH-OR²-OCOR²-OSO₂R² or (-O-)_{1/2}. Y³ expresses -OH-NH₂ or -NHR². Y⁴ expresses a halogen atom. R¹ expresses an aliphatic hydrocarbon group of saturation or an unsaturation an aromatic hydrocarbon group or a heterocycle group. R² expresses an aliphatic hydrocarbon group of the carbon numbers 1-20 an aromatic hydrocarbon group or a heterocycle group. m and n express an integer of 1-3.

[Claim 2] The optical semiconductor electrode according to claim 1 whose compound expressed with either formula (I) (II) and (III) is a compound expressed with either following formula (IV) and (V).

Y⁴-R¹-COY⁵ Among (IV) however said formula (IV) Y⁴ and Y⁵ express a halogen atoms for these may be mutually the same and may differ. R¹ expresses an aliphatic hydrocarbon group of saturation or an unsaturation an aromatic hydrocarbon group or a heterocycle group. Y⁴-R¹-NCO Y⁴ expresses a halogen atom among (V) however said formula (V). R¹ expresses an aliphatic hydrocarbon group of saturation or an unsaturation an aromatic hydrocarbon group or a heterocycle group.

[Claim 3] The optical semiconductor electrode according to claim 1 or 2 by which a pigment compound is expressed with either following formula (VI) (VII) (VIII) (IX) (X) (XI) (XII) and (XIII).

Formula (VI) [Formula 1]

Said formula (VI) NakaR⁴R⁵ and R⁶ A hydrogen atom a halogen atom-NO₂-OH the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced or the aromatic hydrocarbon group that may be replaced is expressed and these may be mutually the same and may differ. R⁷ expresses the aliphatic hydrocarbon group of a hydrogen atom or the carbon numbers 1-10. Z¹ expresses a hydrogen atom-NH₂-NHR⁸-OH or -COOH. R⁸ expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. m expresses 1 2 3 or 4. n expresses 0 1 or 2.

Formula (VII) [Formula 2]

Said formula (VII) NakaR¹¹R¹²and R¹³A hydrogen atom a halogen atom-NO₂-OH the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced or the aromatic hydrocarbon group that may be replaced is expressed and these may be mutually the same and may differ. R¹⁴ and R¹⁵ express a hydrogen atom the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced or the aromatic hydrocarbon group that may be replaced as for these may be mutually the same and may differ. R¹⁶ expresses the aliphatic hydrocarbon group of a hydrogen atom or the carbon numbers 1-10. Z² expresses a hydrogen atom-NH₂-NHR¹⁷-OH or -COOH. R¹⁷ expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. X¹⁻ expresses a counter ion. m expresses 1 or 2. n expresses 0 or 2. However when all of R¹⁴R¹⁵and R¹⁶ are bases other than a hydrogen atom Z² expresses -NH₂-NHR¹⁶-OH or -COOH and n expresses 1 or 2. Formula (VIII) [Formula 3]

M² expresses the atom of FeRu or Os among said formula (VIII). X² expresses a halogen atom-OH-CN or -SCN. R²¹ - R²⁴ A hydrogen atom a halogen atom-NO₂- Express COOH-OH-NH₂-NHR²⁵ the aliphatic hydrocarbon group of the carbon numbers 1-10 the aromatic hydrocarbon group that may be replaced or a heterocycle group and these It may be mutually the same and may differ and at least one of R²¹ - the R²⁴ expresses one chosen from -COOH-OH-NH₂-NHR²⁵ or a pyridyl group. R²⁵ expresses the basis of the carbon numbers 1-4 which may be replaced aliphatic hydrocarbon or an aromatic hydrocarbon group. Formula (IX) [Formula 4]

M³ expresses an atom of FeRu or Os among said formula (IX). X³ expresses a halogen atom-SO₄-ClO₄-OH-CN or -SCN. n expresses 0 or 2. R³¹ - R³⁶ A hydrogen atom a halogen atom-NO₂- Express COOH-OH-NH₂-NHR³⁷ an aliphatic hydrocarbon group of the carbon numbers 1-10 an aromatic hydrocarbon group or a heterocycle group and these It may be mutually the same and may differ and at least one of R³¹ - the R³⁶ expresses one chosen from -COOH-OH-NH₂-NHR³⁷ or a pyridyl group. R³⁷ expresses an aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced or an aromatic hydrocarbon group. Formula (X) [Formula 5]

M⁴ expresses the atom of FeRu or Os among said formula (X). R⁴¹ - R⁵¹ A hydrogen atom a halogen atom-NO₂- Express COOH-OH-NH₂-NHR⁵² the aliphatic hydrocarbon group of the carbon numbers 1-10 an aromatic hydrocarbon group or a heterocycle group and these It may be mutually the same and may differ and at least one of R⁴¹ - the R⁵¹ expresses one chosen from -COOH-OH-NH₂-NHR⁵² or a pyridyl group. R⁵² expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced or an aromatic hydrocarbon group.

Formula (XI) [Formula 6]

Said formula (XI) Naka and M⁵ express

H₂MgTiOVOMnFeConickelCuZnGaOHGaClInClor SnO. R⁶¹ - R⁶⁴ A hydrogen atom a halogen atom-NO₂- Express COOH-OH-NH₂-NHR⁶⁵ the aliphatic hydrocarbon group of the carbon numbers 1-10 the aromatic hydrocarbon group that may be replaced or a heterocycle group and these It may be mutually the same and may differ and at least one of R⁶¹ - the R⁶⁴ expresses one chosen from -COOH-OH-NH₂ or -NHR⁶⁵. R⁶⁵ expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced or an aromatic hydrocarbon group. k l m and n express 1 or 2.

Formula (XII) [Formula 7]

Said formula (XII) Naka and M⁶ express H₂MgZnnickelCoCu or Pd. R⁷¹ - R⁷⁸ express a hydrogen atom a halogen atom a hydroxy group an alkoxy group of the carbon numbers 1-4 which may be replaced an aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced or an aromatic hydrocarbon group that may be replaced. A¹ - A⁴ express an aromatic hydrocarbon group or a heterocycle group which may be replaced and these at least one expresses a phenyl group replaced by -NH₂-NHR⁷⁹-OH or -COOH or a pyridyl group. R⁷⁹ expresses an aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced or an aromatic hydrocarbon group. Formula (XIII) [Formula 8]

A⁵ expresses the aromatic hydrocarbon group replaced by -NH₂-NHR⁸¹-OH-COOH or a pyridyl group an aliphatic hydrocarbon group or a pyridyl group among said formula (XIII). R⁸¹ expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced or an aromatic

hydrocarbon group.

[Claim 4]The optical semiconductor electrode according to any one of claims 1 to 3 whose semiconductor is titanium oxide.

[Claim 5]A photoelectric conversion device which has at least a connecting means which connects an electrode of a couple immersed into an electrolytic solutionand an electrode of this couple so that energization is possibleand is characterized by one side of an electrode of this couple being the optical semiconductor electrode according to any one of claims 1 to 4.

[Claim 6]In a photoelectric conversion method of making an electrode of a couple mutually connected so that energization was possible immersed into an electrolytic solutionand producing a photoelectric conversion reaction by irradiating at least one side of an electrode of this coupleA photoelectric conversion methodwherein an electrode which irradiates with said light is the optical semiconductor electrode according to any one of claims 1 to 4.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the optical semiconductor electrode which is efficiently availableand is excellent in photoelectric conversion efficiencystabilityenduranceetc.and can carry out sunlight by low costthe photoelectric conversion device using itand the photoelectric conversion method.

[0002]

[Description of the Prior Art]In recent yearsuse of sunlight attracts attention as an energy resource replaced with fossil fuelssuch as petroleum and coal. As a photoelectric conversion device which transforms light energy into electrical energy directlythe dry type solar cell in which p-n junction was formed on inorganic semiconductorssuch as silicon and gallium arsenideis known widelyand it is already put in practical use as a power supply of the object for remote placesor a portable electronic deviceetc. Howeversince the energy and cost which the manufacture takes are very high in the case of said dry type solar cellthere is a problem that it is difficult to use widely.

[0003]The wet solar cell whichon the other handused the photoelectrochemical reaction which occurs by the interface of a semiconductor and an electrolytic solution as another photoelectric

conversion device which transforms light energy into electrical energy is known. Semiconductors used in said wet solar cells such as titanium oxide and tin oxide as compared with the silicon used in said dry type solar cell gallium arsenide etc. it can manufacture at far low energy and cost and titanium oxide is especially expected as a future energy conversion material from excelling in both sides of a photoelectric transfer characteristic and stability. However it cannot be said that they can use only the ultraviolet radiation which is about 4% of sunlight but their conversion efficiency is high enough since stable optical semiconductor such as titanium oxide have the band gap as large as not less than 3 eV.

[0004] On the surface of this optical semiconductor as sensitizing dye Then organic coloring matters such as cyanine dye and a xanthene dye To make organometallic complexes such as a tris(2,2'-bipyridyl) ruthenium (II) complex adsorb and to carry out spectral sensitization is tried it is known that it is a method effective in improvement in conversion efficiency (T. Osa M. Fujihira Nature. and 264349 (1976).) Brian O'Regan Michael Gratzel Nature 353736 (1991) JP1-220380A etc.

[0005] However in order for the adsorbed coloring matter to tend to **** in the case of the method of making these pigment compounds adsorbing physically on the surface of an optical semiconductor there is a problem that the field of stability and endurance is insufficient. As a method of solving this problem it is gamma. - Via compounds such as aminopropyl triethoxysilane and cyanuric chloride The method to which a pigment compound is made to fix on the surface of an optical semiconductor is proposed (T. Osa M. Fujihira Nature. 264349 (1976) JP5-124964A etc.).

However when it is this method there is a problem that the quantity of a fixable pigment compound is not enough and a photoelectric transfer characteristic is not necessarily good etc. Organic coloring matters such as cyanine dye and a xanthene dye is not enough in respect of stability endurance etc. and on the other hand although organometallic complexes such as an organic ruthenium complex are excellent in fields such as conversion efficiency and stability they have in them the problem of being expensive. Therefore the actual condition is that high conversion efficiency the optical semiconductor electrode cheap at high durability the photoelectric conversion device and the photoelectric conversion method are not yet provided.

[0006]

[Problem(s) to be Solved by the Invention] This invention solves many problems in said former and makes it a technical problem to attain the following purposes. That is an object of this invention is to provide the

optical semiconductor electrode photoelectric conversion device and the photoelectric conversion method of it being efficiently available and excelling in photoelectric conversion efficiency, stability, endurance, etc. and carrying out sunlight by low cost. [0007]

[Means for Solving the Problem] Said The means for solving a technical problem is as follows. Namely a chemical adsorption film by at least one sort of a compound expressed with either following formula (I) and (II) reacted to this substrate and (III) on a substrate of <1> semiconductor. It is an optical semiconductor electrode which has a coloring matter film by at least one sort of a pigment compound which reacts to this chemical adsorption film and can form a covalent bond in this order and is characterized by things.

(Y¹)_mR¹(COY²)_n (Y¹) (I) _mR¹(NCO)_n (Y¹) (II) _mR¹(Y³)_n (III) however said formula (I) (II) and (III) Y¹ expresses halogen atom-OR²-OCOR²-OSO₂R²-COY⁴-COOR² or -(CO)₂O inside. Y² expresses a halogen atom-OH-OR²-OCOR²-OSO₂R² or (-O-)_{1/2}. Y³ expresses -OH-NH₂ or -NHR². Y⁴ expresses a halogen atom. R¹ expresses an aliphatic hydrocarbon group of saturation or an unsaturation, an aromatic hydrocarbon group or a heterocycle group. R² expresses an aliphatic hydrocarbon group, an aromatic hydrocarbon group or a heterocycle group of the carbon numbers 1-20. m and n express an integer of 1-3.

[0008] A compound expressed with either <2> type (I) (II) and (III) is an optical semiconductor electrode given in the above <1> which is a compound expressed with either following formula (IV) and (V).

Y⁴-R¹-COY⁵ Among (IV) however said formula (IV) Y⁴ and Y⁵ express a halogen atom, as for these may be mutually the same and may differ. R¹ expresses an aliphatic hydrocarbon group of saturation or an unsaturation, an aromatic hydrocarbon group or a heterocycle group. Y⁴-R¹-NCO Y⁴ expresses a halogen atom among (V) however said formula (V). R¹ expresses an aliphatic hydrocarbon group of saturation or an unsaturation, an aromatic hydrocarbon group or a heterocycle group.

[0009] <3> pigment compounds are optical semiconductor electrodes given in the above <1> or <2> expressed with either following formula (VI) (VII) (VIII) (IX) (X) (XI) (XII) and (XIII).

[0010] Formula (VI) [Formula 9]

Said formula (VI) NakaR⁴R⁵ and R⁶ A hydrogen atom, a halogen atom-NO₂-OH, an aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced or an aromatic hydrocarbon group that may be replaced is

expressed and these may be mutually the same and may differ. R^7 expresses an aliphatic hydrocarbon group of a hydrogen atom or the carbon numbers 1-10. Z^1 expresses a hydrogen atom- NH_2-NHR^8-OH or $-COOH$. R^8 expresses an aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. m expresses 1 or 4. n expresses 0 or 2.
Formula (VII) [Formula 10]

Said formula (VII) Naka $R^{11}R^{12}$ and R^{13} A hydrogen atom a halogen atom- NO_2-OH the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced or the aromatic hydrocarbon group that may be replaced is expressed and these may be mutually the same and may differ. R^{14} and R^{15} express a hydrogen atom the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced or the aromatic hydrocarbon group that may be replaced as for these may be mutually the same and may differ. R^{16} expresses the aliphatic hydrocarbon group of a hydrogen atom or the carbon number 1-10. Z^2 expresses a hydrogen atom- $NH_2-NHR^{17}-OH$ or $-COOH$. R^{17} expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. X^{1-} expresses a counter ion. m expresses 1 or 2. n expresses 0 or 2. However when all of $R^{14}R^{15}$ and R^{16} are bases other than a hydrogen atom Z^2 expresses $-NH_2-NHR^{16}-OH$ or $-COOH$ and n expresses 1 or 2.
Formula (VIII) [Formula 11]

M^2 expresses the atom of Fe Ru or Os among said formula (VIII). X^2 expresses a halogen atom- $OH-CN$ or $-SCN$. $R^{21} - R^{24}$ A hydrogen atom a halogen atom- NO_2- Express $COOH-OH-NH_2-NHR^{25}$ the aliphatic hydrocarbon group of the carbon numbers 1-10 the aromatic hydrocarbon group that may be replaced or a heterocycle group and these It may be mutually the same and may differ and at least one of $R^{21} - R^{24}$ expresses one chosen from $-COOH-OH-NH_2-NHR^{25}$ or a pyridyl group. R^{25} expresses the basis of the carbon numbers 1-4 which may be replaced aliphatic hydrocarbon or an aromatic hydrocarbon group.
Formula (IX) [Formula 12]

M^3 expresses an atom of Fe Ru or Os among said formula (IX). X^3 expresses a halogen atom- $SO_4-ClO_4-OH-CN$ or $-SCN$. n expresses 0 or 2. $R^{31} - R^{36}$ A hydrogen atom a halogen atom- NO_2- Express $COOH-OH-NH_2-NHR^{37}$ an aliphatic hydrocarbon group of the carbon numbers 1-10 an aromatic hydrocarbon group or a heterocycle group and these It may be mutually the same and may

differ and at least one of R^{31} - the R^{36} expresses one chosen from $-COOH-$
 $OH-NH_2-NHR^{37}$ or a pyridyl group. R^{37} expresses an aliphatic hydrocarbon
 group of the carbon numbers 1-4 which may be replaced or an aromatic
 hydrocarbon group.

Formula (X)

[Formula 13]

M^4 expresses an atom of Fe or Os among said formula (X). R^{41} - R^{51} A
 hydrogen atom a halogen atom $-NO_2-$ Express $COOH-OH-NH_2-NHR^{52}$ an aliphatic
 hydrocarbon group of the carbon numbers 1-10 an aromatic hydrocarbon
 group or a heterocycle group and these It may be mutually the same and may
 differ and at least one of R^{41} - the R^{51} expresses one chosen from $-COOH-$
 $OH-NH_2-NHR^{52}$ or a pyridyl group. R^{52} expresses an aliphatic hydrocarbon
 group of the carbon numbers 1-4 which may be replaced or an aromatic
 hydrocarbon group.

Formula (XI) [Formula 14]

Said formula (XI) Naka and M^5 express

$H_2MgTiOVOMnFeCoNiCuZnGaOHGaClInClor SnO$. R^{61} - R^{64} A hydrogen atom a
 halogen atom $-NO_2-$ Express $COOH-OH-NH_2-NHR^{65}$ the aliphatic hydrocarbon
 group of the carbon numbers 1-10 the aromatic hydrocarbon group that may
 be replaced or a heterocycle group and these It may be mutually the same and
 may differ and at least one of R^{61} - the R^{64} expresses one chosen from -
 $COOH-OH-NH_2$ or $-NHR^{65}$. R^{65} expresses the aliphatic hydrocarbon group of the
 carbon number 1-4 which may be replaced or an aromatic hydrocarbon group.
 k and n express 1 or 2.

Formula (XII) [Formula 15]

Said formula (XII) Naka and M^6 express $H_2MgZnNiCoCuor Pd$. R^{71} - R^{78}
 express a hydrogen atom a halogen atom a hydroxy group the alkoxy group of
 the carbon numbers 1-4 which may be replaced the aliphatic hydrocarbon
 group of the carbon numbers 1-10 which may be replaced or the aromatic
 hydrocarbon group that may be replaced. A^1 - A^4 express the aromatic
 hydrocarbon group or heterocycle group which may be replaced and these at
 least one expresses the phenyl group replaced by $-NH_2-NHR^{79}-OH$ or $-COOH$ or
 a pyridyl group. R^{79} expresses the aliphatic hydrocarbon group of the
 carbon numbers 1-4 which may be replaced or an aromatic hydrocarbon group.
 Formula (XIII) [Formula 16]

A⁵ expresses an aromatic hydrocarbon group replaced by -NH₂-NHR⁸¹-OH-COOH or a pyridyl group an aliphatic hydrocarbon group or a pyridyl group among said formula (XIII). R⁸¹ expresses an aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced or an aromatic hydrocarbon group.

[0011]<4> semiconductors are optical semiconductor electrodes given in either of <3> from the above <1> which is titanium oxide.

[0012]It has at least a connecting means which connects an electrode of a couple immersed into <5> electrolytic solutions and an electrode of this couple so that energization is possible and one side of an electrode of this couple is a photoelectric conversion device characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <4>.

[0013]<6> In a photoelectric conversion method of making an electrode of a couple mutually connected so that energization was possible immersed into an electrolytic solution and producing a photoelectric conversion reaction by irradiating at least one side of an electrode of this couple An electrode which irradiates with said light is the photoelectric conversion method characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <4>.

[0014]

[Embodiment of the Invention] (Optical semiconductor electrode) The chemical adsorption film by at least one sort of a compound expressed with either following formula (I) and (II) to which the optical semiconductor electrode of this invention reacts to this substrate on the substrate of a semiconductor and (III) It has a coloring matter film by at least one sort of the pigment compound which reacts to this chemical adsorption film and can form a covalent bond in this order.

[0015]- Substrate of a semiconductor - As said semiconductor for example Titanium oxide tin oxide Tungstic oxide a zinc oxide indium oxide niobium oxide strontium titanate Silicon gallium arsenide indium phosphorus a cadmium sulfide gallium nitride cadmium selenide gallium phosphorus a cadmium tellurium copper oxides silicon carbide silicon nitride etc. are mentioned. These may be used by an one-sort independent and may use two or more sorts together. Especially in this invention the reasons of a photoelectric transfer characteristic chemical stability manufacture ease etc. to titanium oxide is preferred also in these.

[0016]There is no restriction in particular about the shape of the substrate of said semiconductor structure and a size and it can choose

suitably according to the purpose. For example it may be a substrate which consists only of semiconductors and may be a substrate which forms the coating membrane of a semiconductor on an electrode with publicly known tabular [by the transparent electrode by ITO glass, soda glass etc., platinum, copper, black lead etc.] or mesh state electrode etc. In the case of the latter substrate this coating membrane may be provided the whole surface on said publicly known electrode and may be provided in part.

[0017]- Compound expressed with either formula (I) (II) and (III) - The compound of these is expressed with a following formula.

(Y¹)_mR¹(COY²)_n (Y¹) (I) _mR¹(NCO)_n (Y¹) (II) _mR¹(Y³)_n (III) however said formula (I) (II) and (III) Y¹ expresses halogen atom-OR²-OCOR²-OSO₂R²-COY⁴-COOR² or -(CO)₂O inside. Y² expresses a halogen atom-OH-OR²-OCOR²-OSO₂R² or (-O-)_{1/2}. Y³ expresses -OH-NH₂ or -NHR². Y⁴ expresses a halogen atom. R¹ expresses the aliphatic hydrocarbon group of saturation or an unsaturated aromatic hydrocarbon group or a heterocycle group. R² expresses the aliphatic hydrocarbon group, aromatic hydrocarbon group or heterocycle group of the carbon numbers 1-20. m and n express the integer of 1-3.

[0018] As an example of a compound expressed with said formula (I) the following compounds (I-1 to I-49) -- said formula (II) -- as an example of a compound expressed the following compounds (III-1 - III-12) are suitably mentioned respectively as an example of a compound in which the following compounds (II-1 - II-5) are expressed with said (III).

[0019] Chloroacetic acid [ClCH₂COOH] ... (I-1) chloroacetyl chloride [ClCH₂COC1] ... (I-2) Methyl chloroacetate [ClCH₂COOCH₃] ... (I-3) Ethyl chloroacetate [ClCH₂COOC₂H₅] ... (I-4) 3-chloropropionic acid [ClCH₂COOH] ... (I-5) 3-chloropropionyl chloride [Cl(CH₂)₂COC1] ... (I-6) 3-chloromethyl propionate [Cl(CH₂)₂COOC₂H₅] ... (I-7) 2-chloroethyl propionate [Cl(CH₂)₂COOC₂H₅] ... (I-8) 4-chlorobutanoic acid [Cl(CH₂)₃COOH] ... (I-9) 4-chlorobutyryl chloride [Cl(CH₂)₃COC1] --- (I-10) 4-chloromethyl butyrate [Cl(CH₂)₃COOCH₃] --- (I-11) [0020] 4-ethyl chloroacetate [Cl(CH₂)₃COOC₂H₅] ... (I-12) 8-chlorooctanoyl chloride [Cl(CH₂)₇COC1] --- (I-13) 8-chloromethyl octanoate [Cl(CH₂)₇COCH₃] --- (I-14) 8-chloroethyl octanoate [Cl(CH₂)₇COOC₂H₅] ... (I-15) Bromoacetic acid [BrCH₂COOH] --- (I-16) Bromoacetyl chloride [BrCH₂COC1] ... (I-17) Methyl bromoacetate [BrCH₂COOCH₃] ... (I-18) Ethyl bromoacetate [BrCH₂COOC₂H₅] ... (I-19) 3-bromopropionic acid [Br(CH₂)₂COOH] --- (I-20) 3-bromopropionyl chloride [Br(CH₂)₂COC1] ... (I-21) [0021] 3-bromomethyl propionate [Br(CH₂)₂COOCH₃] ... (I-22) 3-bromoethyl propionate [Br(CH₂)₂COOC₂H₅] ... (I-23) 4-bromobutanoic acid [Br(CH₂)

$\text{COOH}] \dots (\text{I-24}) 4\text{-bromobutyrylchloride } [\text{Br}(\text{CH}_2)_3\text{COCl}] \text{ --- } (\text{I-25}) 4\text{-bromomethyl butyrate } [\text{Br}(\text{CH}_2)_3\text{COOCH}_3] \text{ --- } (\text{I-26}) 4\text{-bromoethyl butylate } [\text{Br}(\text{CH}_2)_3\text{COOC}_2\text{H}_5] \dots (\text{I-27}) 8\text{-bromooctanoic acid } [\text{Br}(\text{CH}_2)_7\text{COOH}] \dots (\text{I-28}) 8\text{-bromooctanoylchloride } [\text{Br}(\text{CH}_2)_7\text{COCl}] \text{ --- } (\text{I-29}) 8\text{-bromomethyl octanoate } [\text{Br}(\text{CH}_2)_7\text{COOCH}_3] \text{ --- } (\text{I-30}) 8\text{-bromoethyl octanoate } [\text{Br}(\text{CH}_2)_7\text{COOC}_2\text{H}_5] \dots (\text{I-31}) \text{iodoacetic acid } [\text{ICH}_2\text{COOH}] \dots (\text{I-32}) [0022] 4\text{-chlorobenzoic acid } [4\text{-ClPhCOOH}] \dots (\text{I-33}) 4\text{-chlorobenzoylchloride } [4\text{-ClPhCOCl}] \dots (\text{I-34}) 4\text{-chloromethyl benzoate } [4\text{-ClPhCOOCH}_3] \dots (\text{I-35}) 3\text{-bromobenzoic acid } [3\text{-BrPhCOOH}] \dots (\text{I-36}) 3\text{-bromobenzoylchloride } [3\text{-BrPhCOCl}] \dots (\text{I-37}) 3\text{-bromobenzoic acid methyl } [3\text{-BrPhCOOCH}_3] \dots (\text{I-38}) 4\text{-bromobenzoic acid } [4\text{-BrPhCOOH}] \dots (\text{I-39}) 4\text{-bromobenzoylchloride } [4\text{-BrPhCOCl}] \dots (\text{I-40}) 4\text{-bromobenzoic acid methyl } [4\text{-BrPhCOOCH}_3] \dots (\text{I-41}) 3\text{-iodobenzoic acid } [3\text{-IPhCOOH}] \dots (\text{I-42}) [0023] 4\text{-iodobenzoic acid } [4\text{-IPhCOOH}] 4\text{-iodomethyl benzoate } [4\text{-IPhCOOCH}_3] \text{ --- } (\text{I-44}) 4\text{- (chloromethyl) Methyl benzoate } [4\text{-(ClCH}_2\text{) PhCOOCH}_3] \text{ --- } (\text{I-45}) 4\text{- (chloromethyl) Benzoylchloride } [4\text{-(ClCH}_2\text{) PhCOCl}] \dots (\text{I-46}) 4\text{- (chloromethyl) Methyl benzoate } [4\text{-(ClCH}_2\text{) PhCOOCH}_3] \text{ --- } (\text{I-47}) 4\text{- (bromomethyl) Benzoylchloride } [4\text{-(BrCH}_2\text{) PhCOCl}] \dots (\text{I-48}) 4\text{- (bromomethyl) Methyl benzoate } [4\text{-(BrCH}_2\text{) PhCOOCH}_3] \text{ --- } (\text{I-49}) \text{Isocyanic acid 2-chloroethyl } [\text{ClCH}_2\text{CH}_2\text{NCO}] \dots (\text{II-1}) \text{isocyanic acid 3-chlorophenyl } [3\text{-ClPhNCO}] \dots (\text{II-2}) [0024] 4\text{-chlorophenyl isocyanate } [4\text{-ClPhNCO}] \dots (\text{II-3}) \text{Isocyanic acid 3-bromophenyl } [3\text{-BrPhNCO}] \dots (\text{II-4}) \text{Isocyanic acid 4-bromophenyl } [4\text{-BrPhNCO}] \dots (\text{II-5}) 4\text{-chloro-1-butanol } [\text{Cl}(\text{CH}_2)_4\text{OH}] \dots (\text{III-1}) 2\text{-bromoethanol } [\text{BrCH}_2\text{CH}_2\text{OH}] \dots (\text{III-2}) 11\text{-bromo-1-undecanol } [\text{Br}(\text{CH}_2)_{11}\text{OH}] \dots (\text{III-3}) 12\text{-bromo-1-dodecanol } [\text{Br}(\text{CH}_2)_{12}\text{OH}] \dots (\text{III-4}) 4\text{-chlorobenzyl alcohol } [4\text{-ClPhCH}_2\text{OH}] \dots (\text{III-5}) 4\text{-chlorophenethyl alcohol } [4\text{-ClPhCH}_2\text{CH}_2\text{OH}] \dots (\text{III-6}) 4\text{-bromophenethyl alcohol } [4\text{-BrPhCH}_2\text{CH}_2\text{OH}] \text{ --- } (\text{III-7}) [0025] 3\text{-chloroaniline } [3\text{-ClPhNH}_2] \dots (\text{III-8}) 4\text{-chloroaniline } [4\text{-ClPhNH}_2] \dots (\text{III-9}) 3\text{-bromoaniline } [3\text{-BrPhNH}_2] \dots (\text{III-10}) 4\text{-bromoaniline } [4\text{-BrPhNH}_2] \dots (\text{III-11}) 4\text{-chlorobenzylamine } [4\text{-ClPhCH}_2\text{NH}_2] \dots (\text{III-12}) \text{ etc. are mentioned. "Ph" expresses a phenyl group among these formulas. These may be used by an one-sort independent and may use two or more sorts together.}$

[0026] Also in these the carboxylate ghosts expressed with following formula (IV) or the isocyanic ester expressed with following formula (V) is preferred in respect of reactivity the stability of the chemical adsorption film formed a mechanical strength etc.

$\text{Y}^4\text{-R}^1\text{-COY}^5 \dots$ Among (IV) however said formula (IV) Y^4 and Y^5 express a halogen atoms for these may be mutually the same and may differ. R^1 expresses the aliphatic hydrocarbon group of saturation or an

unsaturationan aromatic hydrocarbon groupor a heterocycle group.
 $Y^4-R^1-NCO \dots Y^4$ expresses a halogen atom among (V)however said formula (V). R^1 expresses the aliphatic hydrocarbon group of saturation or an unsaturationan aromatic hydrocarbon groupor a heterocycle group.

[0027]- Pigment compound - What is necessary is just what reacts to the compound expressed with either said formula (I) (II) and (III) as said pigment compoundand can form a covalent bondThe compound expressed with either following formula (VI) (VII) (VIII) (IX) (X) (XI) (XII) and (XIII) is mentioned.

[0028]Formula (VI) [Formula 17]

[0029]Said formula (VI) Naka R^4R^5 and R^6 A hydrogen atoma halogen atom- NO_2 -OHan aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replacedor an aromatic hydrocarbon group that may be replaced is expressedand these may be mutually the same and may differ. R^7 expresses an aliphatic hydrocarbon group of a hydrogen atom or the carbon numbers 1-10. Z^1 expresses a hydrogen atom- NH_2-NHR^8-OH or $-COOH$. R^8 expresses an aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. m expresses 123or 4. n expresses 01or 2.

[0030]Formula (VII) [Formula 18]

[0031]Said formula (VII) Naka $R^{11}R^{12}$ and R^{13} A hydrogen atoma halogen atom- NO_2-OH the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replacedor the aromatic hydrocarbon group that may be replaced is expressedand these may be mutually the same and may differ. R^{14} and R^{15} express a hydrogen atomthe aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replacedor the aromatic hydrocarbon group that may be replacedas for thes may be mutually the sameand may differ. R^{16} expresses the aliphatic hydrocarbon group of a hydrogen atom or the carbon number 1-10. Z^2 expresses a hydrogen atom- $NH_2-NHR^{17}-OH$ or $-COOH$. R^{17} expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. X^{1-} expresses a counter ion. m expresses 1 or 2. n expresses 01or 2. Howeverwhen all of $R^{14}R^{15}$ and R^{16} are bases other than a hydrogen atom Z^2 expresses $-NH_2-NHR^{16}-OH$ or $-COOH$ and n expresses 1 or 2.

[0032]Formula (VIII) [Formula 19]

[0033] M^2 expresses the atom of FeRuor Os among said formula (VIII). X^{2-} expresses a halogen atom- $OH-CN$ or $-SCN$. $R^{21} - R^{24}$ A hydrogen atoma halogen

atom-NO₂- COOH-OH-NH₂-NHR²⁵the aliphatic hydrocarbon group of the carbon numbers 1-10the aromatic hydrocarbon group that may be replacedOr a heterocycle group is expressedand these may be mutually the sameand it may differand at least one of R²¹ - the R²⁴ expresses one chosen from - COOH-OH-NH₂-NHR²⁵or a pyridyl group. R²⁵ expresses the basis of the carbon numbers 1-4 which may be replacedaliphatic hydrocarbonor an aromatic hydrocarbon group.

[0034]Formula (IX) [Formula 20]

[0035]M³ expresses an atom of FeRuor Os among said formula (IX). X³ expresses a halogen atom-SO₄-ClO₄-OH-CNor -SCN. n expresses 0lor 2. R³¹ - R³⁶ A hydrogen atoma halogen atom-NO₂- Express COOH-OH-NH₂-NHR³⁷an aliphatic hydrocarbon group of the carbon numbers 1-10an aromatic hydrocarbon groupor a heterocycle groupand theseIt may be mutually the sameand may differand at least one of R³¹ - the R³⁶ expresses one chosen from -COOH-OH-NH₂-NHR³⁷or a pyridyl group. R³⁷ expresses an aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replacedor an aromatic hydrocarbon group.

[0036]Formula (X)

[Formula 21]

[0037]M⁴ expresses the atom of FeRuor Os among said formula (X). R⁴¹ - R⁵¹ A hydrogen atoma halogen atom-NO₂- Express COOH-OH-NH₂-NHR⁵²the aliphatic hydrocarbon group of the carbon numbers 1-10an aromatic hydrocarbon groupor a heterocycle groupand theseIt may be mutually the sameand may differand at least one of R⁴¹ - the R⁵¹ expresses one chosen from -COOH-OH-NH₂-NHR⁵²or a pyridyl group. R⁵² expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replacedor an aromatic hydrocarbon group.

[0038]Formula (XI) [Formula 22]

[0039]Said formula (XI) Naka and M⁵ express

H₂MgTiOVOMnFeConickelCuZnGaOHGaClInClor SnO. R⁶¹ - R⁶⁴ A hydrogen atoma halogen atom-NO₂- Express COOH-OH-NH₂-NHR⁶⁵an aliphatic hydrocarbon group of the carbon numbers 1-10an aromatic hydrocarbon group that may be replacedor a heterocycle groupand theseIt may be mutually the sameand may differand at least one of R⁶¹ - the R⁶⁴ expresses one chosen from - COOH-OH-NH₂or -NHR⁶⁵. R⁶⁵ expresses an aliphatic hydrocarbon group of the

carbon number 1-4 which may be replaced or an aromatic hydrocarbon group.
klmand n express 1 or 2.

[0040]Formula (XII) [Formula 23]

[0041]Said formula (XII) Naka and M⁶ express H₂MgZnnickelCoCuor Pd. R⁷¹ - R⁷⁸ express a hydrogen atom a halogen atom a hydroxy group an alkoxy group of the carbon numbers 1-4 which may be replaced an aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced or an aromatic hydrocarbon group that may be replaced. A¹ - A⁴ express an aromatic hydrocarbon group or a heterocycle group which may be replaced and these at least one expresses a phenyl group replaced by -NH₂-NHR⁷⁹-OH or -COOH or a pyridyl group. R⁷⁹ expresses an aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced or an aromatic hydrocarbon group.

[0042]Formula (XIII) [Formula 24]

[0043]A⁵ expresses the aromatic hydrocarbon group replaced by -NH₂-NHR⁸¹-OH-COOH or a pyridyl group an aliphatic hydrocarbon group or a pyridyl group among said formula (XIII). R⁸¹ expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced or an aromatic hydrocarbon group.

[0044]As a compound expressed with said formula (VI) A compound (VI-1 - 31) shown below as a compound expressed with said formula (VII) A compound (VII-1 - 12) shown below as a compound expressed with said formula (VIII) A compound (VIII-1 - 13) shown below as a compound expressed with said formula (IX) A compound (IX-1 - 11) shown below as a compound expressed with said formula (X) A compound (X-1-4) shown below as a compound expressed with said formula (XI) A compound (XIII-1 - 19) which a compound (XII-1 - 6) which a compound (XI-1 - 15) shown below shows below as a compound expressed with said formula (XII) shows below as a compound expressed with said formula (XIII) is mentioned suitably respectively. These may be used by an one-sort independent and may use two or more sorts together.

[0045]Formula (VI) [Formula 25]

[0046]

[Table 1]

[0047]
[Table 2]

[0048]Formula (VII) [Formula 26]

[0049]
[Table 3]

[0050]Formula (VIII) [Formula 27]

[0051]
[Table 4]

[0052]Formula (IX) [Formula 28]

[0053]
[Table 5]

[0054]Formula (X)
[Formula 29]

[0055]
[Table 6]

[0056]Formula (XI) [Formula 30]

[0057]
[Table 7]

[0058]Formula (XII) [Formula 31]

[0059]

[Table 8]

[0060]Formula (XIII) [Formula 32]

[0061]

[Table 9]

[0062] (Production of an optical semiconductor electrode) Said formula (I) which reacts to this substrate on a substrate of said semiconductor (II) And a process of forming a chemical adsorption film by at least one sort of a compound expressed with either of (III)s For example it can carry out by making a substrate of said semiconductor immersed into a solvent which dissolved at least one sort of a compound expressed with either said formula (I) (II) and (III).

[0063] If a substrate of said semiconductor is made immersed into a solvent which dissolved at least one sort of a compound expressed with either said formula (I) (II) and (III) A chemical bond by a reaction of $-COY^2-NCO$ or $-Y^3$ which is an active group of a base material surface of said semiconductor and a substituent in a compound expressed with either said formula (I) (II) and (III) and $**$ is formed. As a result a chemical adsorption film by at least one sort of a compound expressed with either said formula (I) (II) and (III) is formed in a base material surface of this semiconductor. Then if a suitably selected solvent washes a substrate of this semiconductor an excessive molecule except said chemical adsorption film will be removed.

[0064] As a solvent for dissolving the compound expressed with either said formula (I) (II) and (III) There is no restriction in particular can choose suitably according to the purpose and For example toluene Ester solvents such as hydrocarbon system solvents such as hexane and hexadecane ethyl acetate and n-butyl acetate Ether system solvents such as diethylether and a tetrahydrofuran and dichloromethane Various organic solvents such as alcoholic solvents such as ketone solvents such as halogen system solvents such as 1,1,2-trichloroethane acetone and cyclohexanone ethanol and 1-butanol or these mixed solvents are mentioned. These may be used by an one-sort independent and may use two or more

sorts together.

[0065]Also in these what does not react to the compound expressed with either said formula (I) (II) and (III) in itself is preferred and a hydrocarbon system solvent an ether system solvent or a halogen system solvent is preferred.

[0066]Although it is usually about 1.0×10^{-4} – 1.0 mol/l as concentration in this solvent of the compound expressed with either said formula (I) (II) and (III) 1.0×10^{-4} – $1.0 \times 10^{-2} \text{ mol/l}$ are preferred.

[0067]–COY²–NCO or –Y³ which is an active group of the base material surface of said semiconductor and a substituent in the compound expressed with either said formula (I) (II) and (III)***** can be performed at the temperature below a room temperature or the boiling point of said solvent and an adequate amount in addition its ** are good in acid or a base as a catalyst if needed in that case. It is also good to perform heat treatment acid treatment plasma treatment hot water processing ozonization etc. to the substrate of said semiconductor and to introduce an active layer into it beforehand before said reaction in the base material surface of this semiconductor.

[0068]The process of forming the coloring matter film by at least one sort of said pigment compound which can form a covalent bond in response to said chemical adsorption film top with this chemical adsorption film can be performed when said chemical adsorption film for example immerses the substrate formed in the surface into the solution which dissolved this pigment compound in the solvent. A proper quantity of the acid marginal controlled substances metallic compound etc. may be added as a catalyst in that case.

[0069]If the substrate with which said chemical adsorption film was formed in the surface is made immersed into the solution which dissolved said pigment compound in the solvent with the catalyst this pigment compound will react it to the base material surface of said semiconductor via this chemical adsorption film and it is fixed.

[0070]Said formula As a solvent which dissolves the pigment compound expressed with either (VI) – (XIII) For example ester solvents such as hydrocarbon system solventssuch as toluene hexane and hexadecane and ethyl acetate Ether system solventssuch as diethyl ether and a tetrahydrofuran and dichloromethane Ketone solvents such as halogen system solventssuch as 1,1,2-trichloroethane acetone and cyclohexanone Various organic solventssuch as amide system solventssuch as alcoholic solvents such as ethanol and 1-butanol N,N-dimethylformamide and N-methyl pyrrolidone or these mixed solvents are mentioned. These may be used by an one-sort independent and may use two or more sorts together.

[0071]Also in thesesufficient solubility is shown to said pigment compoundand it does not react in itselfAnd what does not react to the formed chemical adsorption film in itself is preferredand amide system solventssuch as halogen system solventssuch as ether system solventssuch as hydrocarbon system solventssuch as tolueneand a tetrahydrofuranand dichloromethaneand N.N-dimethylformamideetc. are preferred.

[0072]Although the reaction of said pigment compound to the base material surface of said semiconductor may be performed at a room temperatureit may heat to the temperature below the boiling point of a solvent if needed.

[0073]Although it can choose suitably as content of said pigment compound in said solution according to a processing condition etc.it is usually about 0.01-1 weight section to said solvent 100 weight section.

[0074]The optical semiconductor electrode of this invention produced by making it above can be used conveniently for the following photoelectric conversion devices and photoelectric conversion methods of this invention.

[0075] (Photoelectric conversion device) The photoelectric conversion device of this invention has at least a connecting means which connects the electrode of the couple immersed into an electrolytic solutionand the electrode of this couple so that energization is possible. Said photoelectric conversion device may be provided with apparatus suitably selected according to the purpose etc. outside the electrode of said coupleand said connecting means.

[0076]-A pair of electrodes - One side in the electrode of said couple is an optical semiconductor electrode of said this inventionand another side is a counterelectrode. As said counterelectrodeif electrochemically stablethere will be no restriction in particularand according to the purposeit can choose from a publicly known thing suitablyfor examplecan choose from transparent electrodessuch as flat electrodessuch as platinumgoldand black leador ITO glassand Nesa glassetc. suitably according to the purpose.

[0077]- Connecting means - As long as it has a function in which the electrode of said couple can be connected as said connecting means so that energization is possiblethere is no restriction in particular and can choose suitably according to the purposebut. For examplethe wire rod which consists of conductive materialssuch as a publicly known leadvarious metalcarbonand a metallic oxidein itselfa platea printed filmor a vacuum evaporation film is mentioned. This connecting means is connected to the electrode of said couple so that energization is possible. The photoelectric conversion device of the above this

invention can be used conveniently for the photoelectric conversion method of the following this inventions.

[0078] (The photoelectric conversion method) The photoelectric conversion method of this invention makes an electrolytic solution immerse the electrode of the couple mutually connected so that energization was possible and produces a photoelectric conversion reaction by irradiating at least one side of the electrode of this couple. Those in the electrode of said couple who irradiate with light are the optical semiconductor electrodes of said this invention and another side is said counterelectrode. Said connecting means can be used for connecting the electrode of this couple so that energization is possible. For this reason as an electrode of said couple mutually connected so that energization was possible the photoelectric conversion device of said this invention can be used.

[0079] - Electrolytic solution - Although there is no restriction in particular and it can choose suitably as said electrolytic solution For examples salt such as potassium chloride a lithium chloride potassium carbonate and tetraethylammonium perchlorate Nonaqueous solvent solution such as solutions such as acid such as alkali such as sodium hydroxide and potassium carbonate sulfuric acid and chloride or these mixtures or alcohol and propylene carbonate etc. are mentioned. These may be used by an one-sort independent and may use two or more sorts together. In this invention the compound in which it is the purpose of attaining stabilization of the photoelectric current characteristic and also potassium iodide p-benzoquinone etc. produce an oxidation-reduction reaction reversibly may be added to said electrolytic solution.

[0080] (Photoelectric conversion reaction) In the photoelectric conversion device and the photoelectric conversion method of this invention a photoelectric conversion reaction can be produced as follows. That is the above-mentioned electrode i.e. said optical semiconductor electrode and said counterelectrode of a couple are first immersed into said nature solution of an electric field. Next this optical semiconductor electrode is irradiated with the monochromatic light of a 300-650-nm wavelength band the white light which includes one in this wavelength band of zones or multicolor light. Then light energy is transformed into electrical energy in this optical semiconductor electrode. At this time it is changed into electrical energy very efficiently to the light energy of the visible light of not only the ultraviolet radiation of the wavelength band below 300-400 nm but a 400-650-nm wavelength band.

[0081] Even the visible light which cannot be used with metallic-oxide

independentsuch as titanium oxideby using said optical semiconductor electrode in this invention can use effectivelyAs a resultsynthetic use of lightssuch as sunlightis attained and light energiessuch as sunlightcan be transformed into electrical energy at high efficiency. And in said optical semiconductor electrode to be usedsince said pigment compound stuck to the surface firmlyand has combined with it and it is not easily desorbed from this optical semiconductor electrode the characteristic of this optical semiconductor electrode is stabilized for a long period of timecan be maintainedand can always perform a photoelectric conversion reaction efficiently.

[0082]

[Example]Hereafteralthough the example of this invention is describedthis invention is not limited to these examples at all.

[0083] (Example 1)

- 25 ml of production-alt. titanitic acid tetraisopropyl of the optical semiconductor electrode was gradually added into the mixed solution of 150 ml of deionized waterand the concentrated nitric acid 1.54g (specific gravity: 1.38)agitating violently. Temperature up was carried out to 80 **continuing churning furthermorechurning was continued at the temperature for 8 hoursand the milky stable titanium oxide colloidal solution was obtained. The above operation was performed under the dry nitrogen air current. This colloidal solution was condensed until 40 ml of viscous fluids remained at 30 ** under decompression of 30mmHg. In this waythe obtained viscous fluid was used as the titanium oxide colloidal solution.

[0084]Said titanium oxide colloidal solution was coated with the spin coat method on ITO/glass base material as an electrodeand was calcinated at 500 ** for 1 hour. This operation was repeated 3 times and the titanium oxide enveloping layer about 0.3 micrometer thick was formed on this ITO/glass base material. When the crystal structure of the obtained titanium oxide enveloping layer was checked with the X-ray diffraction methodit was checked that it is a mixture of an anatase and a rutile type.

[0085]Said titanium oxide enveloping layer formed ITO/glass base material to the mixed solvent (volume ratio 4:1) of n-hexadecane and a carbon tetrachloride. After being immersed for 2 hours into the solution (concentration: 1×10^{-3} mol/l) which dissolved 4-(bromomethyl) benzoylchloride (compound expressed with said I-48)n-hexadecane and acetone fully washed and natural seasoning was carried out for 30 minutes under a nitrogen atmosphere. Thenit heated for 30 minutes at 80 **and the chemical adsorption film by 4-(bromomethyl) benzoylchloride

(compound expressed with said I-48) was formed in the surface of said titanium oxide enveloping layer. The reaction in this case was shown in drawing 1.

[0086]The surface of this chemical adsorption film was observed using X linear-light electronic spectral device (the product made by VGESCALAB-220i). The measurement result by X linear-light electronic spectral device was shown in drawing 2.

[0087]NextITO/glass base material by which said chemical adsorption film was formed in the surfaceBis(22-bipyridine 44'-dicarboxylic acid)ruthenium (II) It was immersed in the dimethylformamide solution (concentration: 5×10^{-4} mol/l) of dithiocyanate (compound expressed with said VIII-7) and was made to react at 90 ** for 24 hours. Thenby acetone and ethanolit fully washed and natural seasoning was carried out for 30 minutes. As a resultthe coloring matter film by bis(22-bipyridine 44'-dicarboxylic acid)ruthenium (II) dithiocyanate (compound expressed with said VIII-7) was formed on said chemical adsorption film and the surface was assuming transparent and light purple. The reaction in this case was shown in drawing 3.

[0088]The surface of this coloring matter film was observed using X linear-light electronic spectral device (the product made by VGESCALAB-220i). The measurement result by X linear-light electronic spectral device was shown in drawing 4. When the ultraviolet-rays visible absorption spectrum of this coloring matter film is measured as it is shown in drawing 5 it is bis(22-bipyridine 44'-dicarboxylic acid)ruthenium (II). The almost same spectral shape as the ethanol solution of dithiocyanate (compound expressed with said VIII-7) was shown. From the above result it is bis(22-bipyridine 44'-dicarboxylic acid)ruthenium (II). A dithiocyanate (compound expressed with said VIII-7) molecule 4 - (bromomethyl) Being fixed on said titanium oxide enveloping layer via a benzoylchloride (compound expressed with said I-48) molecule was checked.

[0089]Then the lead 7 was connected using what was obtained by the above on the ITO layer portion in which the titanium oxide enveloping layer is not formed the substrate end and the terminal area of the lead 7 were covered with the epoxy resin and the optical semiconductor electrode as shown in drawing 6 was produced. the optical semiconductor electrode 1 shown in drawing 6 -- the glass base material 2 top -- the ITO layer 3 and the titanium oxide enveloping layer 4 -- and The chemical adsorption film 5 by 4-(bromomethyl) benzoylchloride (compound expressed with said I-48) and bis(22-bipyridine 44'-dicarboxylic acid)ruthenium (II) the coloring matter film 6 by dithiocyanate (compound expressed with said

VIII-7). Laminating in this order the end of these lamination sides and the terminal area with the lead 8 were covered with the epoxy resin as the adhesive agent 7 and have adhered with it.

[0090]- The optical semiconductor electrode 1 produced as mentioned above as shown in production-drawing 7 of a photoelectric conversion device. The platinum electrode selected as the counter electrode 9 and the saturated Calomel electrode selected as the reference electrode 10 were immersed in the electrolytic solution 11 in the transparent glass cell 13. Each electrode was connected to the potentiostat 12 using the lead 8 as a connecting means and the photoelectric conversion device was produced. As said electrolytic solution 11, 0.1M sodium sulfate / 0.02M potassium iodide solution was used. The lead 8 is connected to each electrode and energization has become possible. The lead 8 is accommodated in the glass tube. As the reference electrode 10, this photoelectric conversion device is equipped with the saturated calomel electrode so that energization is possible. The photoelectric conversion device was produced by the above.

[0091]- holding in the photoelectric conversion device obtained by more than photoelectric conversion reaction -- so that the potential of said optical semiconductor electrode may be set to 0V to said reference electrode -- white light (the xenon lamp of 500W.) It irradiated with illumination 4000lux or 550-nm monochromatic light (1 mW/cm²) from the back side of said optical semiconductor electrode. The value of the photoelectric current by the photoelectric conversion reaction produced at this time was measured with the potentiostat. The measurement result was shown in Table 10.

[0092] (Example 2) In Example 1 it is bis(2,2'-bipyridine 4,4'-dicarboxylic acid) ruthenium (II). Dithiocyanate (compound expressed with said VIII-7) Like Example 1 the outside replaced with 4-carboxy-2',4',5',7'-tetraiodofluorescein (compound expressed with said VI-8) produced the optical semiconductor electrode and the photoelectric conversion device respectively produced the photoelectric conversion reaction and measured photoelectric current. The measurement result was shown in Table 10.

[0093] (Example 3) In Example 1 it is bis(2,2'-bipyridine 4,4'-dicarboxylic acid) ruthenium (II). Dithiocyanate (compound expressed with said VIII-7) Rhodamine 6G (compound expressed with said VII-7) Like Example 1 the outside replaced with produced the optical semiconductor electrode and the photoelectric conversion device respectively produced the photoelectric conversion reaction and measured photoelectric current. The measurement result was shown in Table 10.

[0094] (Example 4) In Example 1 it is bis(22-bipyridine 44'-dicarboxylic acid)ruthenium (II). Dithiocyanate (compound expressed with said VIII-7) Bis(22'-bipyridine) (22'-bipyridine 44'-dicarboxylic acid) ruthenium (II) the outside replaced with dichloride (compound expressed with said IX-5) Like Example 1 the optical semiconductor electrode and the photoelectric conversion device were produced respectively the photoelectric conversion reaction was produced and photoelectric current was measured. The measurement result was shown in Table 10.

[0095] (Example 5) In Example 1 it is bis(22-bipyridine 44'-dicarboxylic acid)ruthenium (II). Dithiocyanate (compound expressed with said VIII-7) Like Example 1 the outside replaced with the tetra(n-butyl) ammonium salt of the compound expressed with said X-1 produced the optical semiconductor electrode and the photoelectric conversion device respectively produced the photoelectric conversion reaction and measured photoelectric current. The measurement result was shown in Table 10.

[0096] (Example 6) In Example 1 it is bis(22-bipyridine 44'-dicarboxylic acid)ruthenium (II). Dithiocyanate (compound expressed with said VIII-7) (Tetracarboxy phthalocyaninato) Like Example 1 the outside replaced with nickel (II) (compound expressed with said XI-10) produced the optical semiconductor electrode and the photoelectric conversion device respectively produced the photoelectric conversion reaction and measured photoelectric current. The measurement result was shown in Table 10.

[0097] (Example 7) In Example 1 it is bis(22-bipyridine 44'-dicarboxylic acid)ruthenium (II). Dithiocyanate (compound expressed with said VIII-7) meso-porphyrin 44' 4" 4'''-tetra benzoic acid (compound expressed with said XII-1) Like Example 1 the outside replaced with produced the optical semiconductor electrode and the photoelectric conversion device respectively produced the photoelectric conversion reaction and measured photoelectric current. The measurement result was shown in Table 10.

[0098] (Example 8) In Example 1 it is bis(22-bipyridine 44'-dicarboxylic acid)ruthenium (II). Dithiocyanate (compound expressed with said VIII-7) (44' 4" and 4'''-tetra pyridyl)-meso-porphyrin (compound expressed with said XII-6) Like Example 1 the outside replaced with produced the optical semiconductor electrode and the photoelectric conversion device respectively produced the photoelectric conversion reaction and measured photoelectric current. The measurement result was shown in Table 10.

[0099] (Example 9) In Example 1 it is bis(22-bipyridine 44'-dicarboxylic

acid)ruthenium (II). Dithiocyanate (compound expressed with said VIII-7)NN'-screw (2'-carboxyethyl) -34910-perylene 18-diimidotetracarboxylic acid (compound expressed with said XIII-2) The outside replaced with tetra(n-butyl) ammonium saltLike Example 1the optical semiconductor electrode and the photoelectric conversion device were producedrespectivelythe photoelectric conversion reaction was producedand photoelectric current was measured. The measurement result was shown in Table 10.

[0100] (Example 10) In Example 14-(bromomethyl) benzoylchloride (compound expressed with said I-48)To isocyanic acid 2-chloroethyl (compound expressed with said II-1). Bis(22-bipyridine 44'-dicarboxylic acid)ruthenium (II) dithiocyanate (compound expressed with said VIII-7)The outside replaced with rhodamine 6G (compound expressed with said VII-7) produced the optical semiconductor electrode and the photoelectric conversion device like Example 1and measured the value of photoelectric current. The measurement result was shown in Table 10.

[0101] (Example 11) In Example 14-(bromomethyl) benzoylchloride (compound expressed with said I-48)To isocyanic acid 2-chloroethyl (compound expressed with said II-1). Bis(22-bipyridine 44'-dicarboxylic acid)ruthenium (II) dithiocyanate (compound expressed with said VIII-7)The outside replaced with NN'-bis(6'-aminohexyl)-34910-perylene 18-diimidotetracarboxylic acid (compound expressed with said XIII-8) produced the optical semiconductor electrode and the photoelectric conversion device like Example 1and measured the value of photoelectric current. The measurement result was shown in Table 10.

[0102] (Comparative example 1) In Example 1outside which did not combine a pigment compound on said titanium oxide enveloping layer is made to be the same as that of Example 1 not using 4-(bromomethyl) benzoylchloride (compound expressed with said I-48)The optical semiconductor electrode and the photoelectric conversion device were producedrespectivelythe photoelectric conversion reaction was producedand photoelectric current was measured. The measurement result was shown in Table 10.

[0103] (Comparative example 2) In Example 1the outside which did not form the chemical adsorption film by 4-(bromomethyl) benzoylchloride (compound expressed with said I-48)Like Example 1the optical semiconductor electrode and the photoelectric conversion device were producedrespectivelythe photoelectric conversion reaction was producedand photoelectric current was measured. The measurement result was shown in Table 10.

[0104] (Comparative example 3) In Example 1outside which replaced with gamma-aminopropyl triethoxysilane 4-(bromomethyl) benzoylchloride

(compound expressed with said I-48) is made to be the same as that of Example 1. The optical semiconductor electrode and the photoelectric conversion device were produced respectively. The photoelectric conversion reaction was produced and photoelectric current was measured. The measurement result was shown in Table 10.

[0105]

[Table 10]

[0106]

[Effect of the Invention] According to this invention many problems in said former are solvable. According to this invention the optical semiconductor electrode, photoelectric conversion device and the photoelectric conversion method of it being efficiently available and excelling in photoelectric conversion efficiency, stability, endurance etc. and carrying out sunlight by low cost can be provided.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is a key map for explaining an example in the state where the chemical adsorption film was formed in the base material surface of a semiconductor.

[Drawing 2] Drawing 2 is 4 on the titanium oxide enveloping layer formed in the surface of ITO/glass base material as a substrate of a semiconductor. - (bromomethyl) It is data of X linear-light electron spectrum of the base material surface of the semiconductor concerned after combining benzoylchloride.

[Drawing 3] Drawing 3 is a key map for explaining an example in the state where the pigment compound was fixed to the base material surface of a semiconductor via the chemical adsorption film.

[Drawing 4] 4 which combined drawing 4 on the titanium oxide enveloping layer - (bromomethyl) On the surface of benzoylchloride. It is data of X linear-light electron spectrum of the base material surface of the semiconductor concerned which combined bis(2,2'-bipyridine 4,4'-dicarboxylic acid)ruthenium (II) dithiocyanate (compound expressed with said VIII-7).

[Drawing 5] Drawing 5 is data of the ultraviolet and visible absorption spectrum of the optical semiconductor electrode in Example 1.

[Drawing 6] Drawing 6 is a section approximate account figure of the optical semiconductor electrode in Example 1.

[Drawing 7] Drawing 7 is an approximate account figure of the photoelectric conversion device in Example 1.

[Description of Notations]

- 1 Optical semiconductor electrode
 - 2 Glass base material
 - 3 ITO layer
 - 4 Titanium oxide enveloping layer
 - 5 Chemical adsorption film
 - 6 Coloring matter film
 - 7 Adhesive agent
 - 8 Lead
 - 9 Counterelectrode
 - 10 Reference electrode
 - 11 Electrolytic solution
 - 12 Potentiostat
 - 13 Glass cell
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